Defects, Quasibound States, and Quantum Conductance in Metallic Carbon Nanotubes

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The effects of impurities and local structural defects on the conductance of metallic carbon nanotubes are calculated using an *ab initio* pseudopotential method within the Landauer formalism. Substitutionally doped boron or nitrogen produces quasibound impurity states of a definite parity and reduces the conductance by a quantum unit ($2e^2/h$) via resonant backscattering. These resonant states show strong similarity to acceptor or donor states in semiconductors. The Stone-Wales defect also produces quasibound states and exhibits quantized conductance reduction. In the case of a vacancy, the conductance shows a much more complex behavior than the prediction from the widely used π-electron tight-binding model.

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Carbon nanotubes, a new structural form of carbon discovered by Iijima [1], have great potential for nanoscale electronic device applications because of their extraordinarily small diameter and versatile electronic properties [2–4]. Their conducting characteristics have been studied extensively. The conductance of a one-dimensional conductor is known to have an especially simple form according to Landauer's formula, namely, the number of conducting channels (two, at the Fermi level in the case of single wall nanotubes) times the conductance quantum, $G_0 = 2e^2/h$ [5]. This quantized conductance would be changed in the presence of local structural defects or impurities. Much theoretical effort has been made to solve the problem of conductance with defects, mostly with the tight-binding method [5,6]. Here, in order to obtain the conductance taking into account the defect-induced atomic relaxation and self-consistent electronic redistribution properly, we have performed *ab initio* nonlocal pseudopotential calculations. Substitutional impurities, Stone-Wales defects (pentagon-heptagon-pair defects), and vacancies are studied. We find that the *ab initio* results are sometimes quite different from the simple one-p-orbital tight-binding calculations. For example, in the presence of a vacancy, the position of the conductance dip is shifted in energy by a large amount and, more importantly, there exists more than one dip with different physical origins unlike the predictions of the π-orbital tight-binding model. We find that in general the reduction of the conductance by a defect is itself quantized. This phenomenon will be explained in terms of a resonant backscattering by quasibound defect states of a definite parity.

An (n, n) (armchair-type) carbon nanotube is a metallic nanowire with two linear electronic energy bands which cross at the Fermi level (E_F) and contribute two conductance quanta ($=4e^2/h$) to the conductance when the tube is defectless [2]. In this work, we consider a $(10, 10)$ carbon nanotube with different local defects and calculate its intrinsic conductance [7] with an *ab initio* nonlocal pseudopotential method. The supercell of 10–20 Å in each dimension is used to calculate the perturbed potential (by a defect) self-consistently which is in general of short range. The electronic wave functions are calculated using the wave function matching method [8] throughout an infinitely long tube with a defective region at the center. The cutoff energy for the plane-wave expansion of the wave function is 35 Ry and the atomic positions are relaxed according to calculated forces. Conductance is obtained from the multichannel extension of the Landauer formalism [9], $G(E) = G_0 \,\mathrm{Tr}(t^\dagger t)$, where t is the transmission matrix.

The calculated conductance of a $(10, 10)$ carbon nanotube with a boron impurity is presented in Fig. 1. A feature of immediate interest is that the conductance is virtually unchanged at E_F for a neutral nanotube ($E_F = 0$); that is, the impurity potential does not scatter incoming electrons at this energy. On the other hand, we observe two dips in conductance below E_F. The amount of the reduction at the upper dip is 1 G_0 and its shape is approximately Lorentzian in agreement with the scattering wave analysis using the Green's function method [10]. In fact, the overall structures of the conductance may be well described by a superposition of two Lorentzian dips with a depth of 1 G_0 each. The upper dip is caused by an approximate half reflection from states of both of the conducting bands, 47% of the π band and 53% of the π^* band. Because a single impurity breaks the mirror symmetry planes containing the tube axis [11], an eigenchannel [12] is a mixture of the π and π^* bands. An electron in an eigenchannel here is either completely reflected or completely transmitted.

Associated with the two conductance dips, the local density of states (LDOS) around the boron impurity shows two peaks arising from the presence of quasibound states (Fig. 1). The lower peak is too close ($\lesssim$1 meV) to be seen

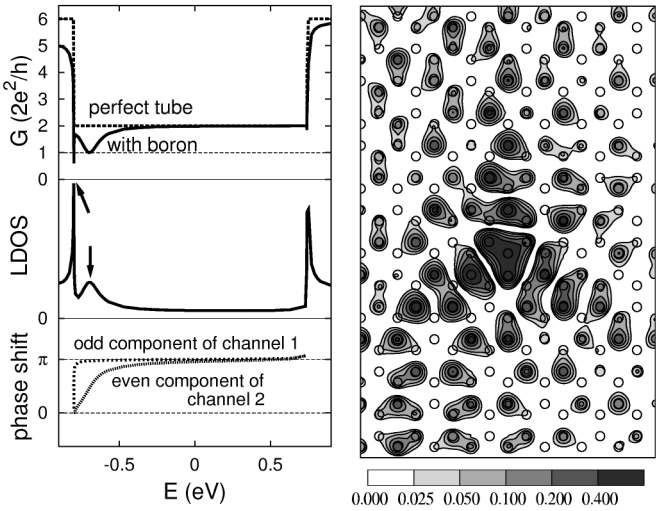

FIG. 1. Effects of the boron substitutional impurity on conductance in the $(10, 10)$ carbon nanotube. The conductance as a function of the incident energy E shows two dips. The local density of states (LDOS) and the scattering phase shifts of the two eigenchannels show peaks (indicated by arrows) and rapid changes, respectively, associated with the dips in the conductance. The charge density contour plot shows the electronic state at -0.70 eV incident from the left and totally reflected by the quasibound state at the energy. The horizontal axis is along the tube axis and the vertical axis is along the circumference.

separately from the peak originating from the van Hove singularity of the lower subbands. The spatial extent of the quasibound state at the upper energy peak is approximately 10 Å (right panel of Fig. 1) and that at the lower-energy peak is roughly 200 Å (not shown). While a perfect tube has mirror planes perpendicular to the tube axis as well as parallel to it, the substitution of a boron atom preserves only one mirror plane containing the boron atom and perpendicular to the tube axis. The two quasibound states are parity eigenstates with respect to this mirror plane; the lower one (narrower peak) has odd parity and the upper one (broader peak) has even parity. A propagating state along the tube may be expressed as a sum of 50% of an even state and 50% of an odd state converging onto the impurity. The even component may be scattered (i.e., phase shifted) by the quasibound state of even parity only and the odd component by that of odd parity only. We calculate the phase shift for each parity component for a particular eigenchannel using the expression

$$\theta = \frac{1}{2}\,\mathrm{Im}\log\mathrm{Det}(S)\,, \tag{1}$$

where S is the scattering matrix [13]. For the eigenchannel that is reflected by the lower quasibound state (channel 1), the phase of the odd parity component changes rapidly as the energy sweeps past the lower quasibound state level, and its value passes through $\pi/2$ at the peak of the quasibound state as in Fig. 1. The phase of the even component of this channel is unchanged and not shown. Total reflection occurs by a destructive interference between the even and the odd component. A similar change occurs to the phase of the even parity component of the other eigenchannel (channel 2) that is reflected by the upper quasibound state. The total phase shift across a quasibound state is π in each case in agreement with the Friedel sum rule [13,14]. Figure 1 shows the charge density for the totally reflected state at -0.7 eV. Note that the total charge density does not look symmetric with respect to the mirror plane because the incoming electronic wave function from the left has been added to the mirror symmetric quasibound state.

A nitrogen substitutional impurity has similar effects on conductance, but with its energy structures opposite to the boron case. Figure 2 shows two conductance dips above the Fermi level. The LDOS near the nitrogen impurity shows two peaks corresponding to quasibound states. The upper peak is not well separated from that originating from the van Hove singularity of the upper subbands. The spatial extent of the wave functions is $\lesssim$10 Å at the lower energy peak and $\sim$50 Å at the upper energy peak (not shown). The lower quasibound state has even parity with respect to the mirror plane and the upper one has odd parity. The phase of the scattering matrix changes rapidly as the energy sweeps past a bound state level as in boron.

The quasibound states in the metallic nanotube with boron or nitrogen impurities have a similar physical origin to that of acceptor or donor levels in typical semiconductors or semiconducting nanotubes [15]. The quasibound levels associated with boron are close to the first lower subband (and derived mainly from it) analogous to the acceptor level in semiconductors except that they are in resonance with the continuum of conducting states. Among the two quasibound states, the one with the larger binding

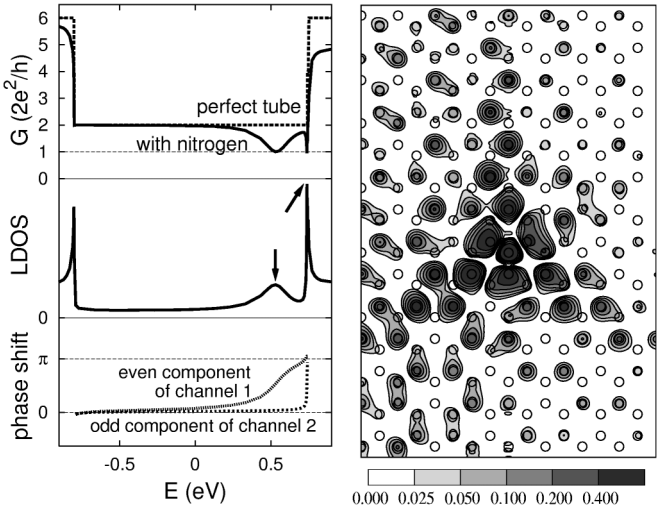

FIG. 2. Effects of the nitrogen substitutional impurity on conductance in the $(10, 10)$ carbon nanotube. The conductance, the LDOS, and the scattering phase shifts of the two eigenchannels are plotted as in Fig. 1. The contour plot shows the totally reflected state at 0.53 eV.

energy (in the hole language) located at 0.1 eV above the first lower subband has even parity and is relatively well localized ($\lesssim$10 Å), reminiscent of an s-like acceptor level. The lower state with a much smaller binding energy has odd parity with a huge spatial extent ($\sim$200 Å), a one-dimensional analog of the p-like acceptor level. Likewise, the quasibound states associated with the nitrogen impurity behave similarly to the donor states in semiconductors.

With a Stone-Wales defect, the conductance has two dips as shown in Fig. 3. Again, the dips are located away from E_F and the conductance close to E_F is not significantly affected by the defect. Our results thus show that the conductance of the metallic (n, n) tube at E_F is quite robust with respect to intratube local defects. The amount of the conductance reduction at the two dips is very close to 1 G_0. In this case, the lower dip is due to an almost complete reflection of the π^* band, whereas the upper dip is due to that of the π band. The pentagon-heptagon-pair defect studied here preserves, in addition to the mirror symmetry plane ($M1$) perpendicular to the tube axis which exists with a single impurity, another mirror plane ($M2$) containing the tube axis. With respect to $M2$, the π band state in the perfect tube is even and the π^* band state is odd. Therefore, the π and π^* bands do not mix and remain as eigenchannels in this defective tube.

The LDOS near the pentagon-heptagon-pair defect in Fig. 3 shows two peaks at the energies corresponding to the conductance dips characteristic of two quasibound states at the defect. The lower quasibound state is odd with respect to $M2$ (i.e., it is a π^* state) but even with respect to $M1$, while the upper quasibound state is even with respect to $M2$ (i.e., a π state) but odd with respect to $M1$. The labeling of the parity (even or odd) for the phase shift in Fig. 3 is with respect to $M1$ as in the previous figures. We note that, if the pentagon-heptagon-pair bonds are tilted with respect to the tube axis, parity should be defined with respect to a 180° rotation.

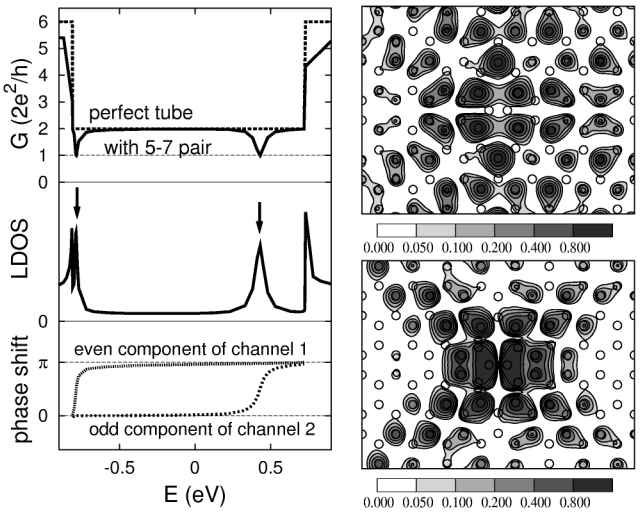

FIG. 3. Effects of the pentagon-heptagon-pair defect on conductance in the $(10, 10)$ carbon nanotube. The conductance, the LDOS, and the scattering phase shifts of the two eigenchannels are plotted as in Fig. 1. The contour plots show the totally reflected states at -0.78 eV (top right) and 0.43 eV (bottom right), respectively.

Another type of the structural defect of interest in carbon nanotubes is the vacancies. With a point (single-atom) vacancy, the conductance shows one broad dip and two very narrow dips as shown in Fig. 4(a). The reduction of conductance at the broad dip is 1 G_0 with approximately half reflection of both π and π^* bands as in the cases for the B and N impurities. The location of the broad dip in the present *ab initio* calculation (-0.4 eV with respect to E_F) is quite different from the result of the widely used tight-binding model that considers only one p electron per carbon atom perpendicular to the tube surface. The tight-binding model predicts a single dip exactly at the Fermi level [5]. However, electron-hole symmetry is no longer valid in the realistic calculation, and the dip position moves. Moreover, we find two other narrow dips near E_F not found in the tight-binding model. The narrow dips originate from resonant scattering by quasibound states derived from the broken σ bonds around the vacancy. The σ bonds between the removed atom and its neighbors are broken, and dangling bonds are produced which are mainly composed of p orbitals *parallel to* the tube surface. Since σ-bond states are orthogonal to the π valence band states, there is very little coupling between them. Among three quasibound states derived from three dangling bonds, one is an s-like bonding state which lies well below the first lower subband (outside the scope of the figure). The other two states are orthogonal to it (i.e., partially antibonding) and give rise to two narrow dips in the figure. Because the interaction among the dangling σ bonds causes a substantial atomic relaxation and there can be more than one metastable atomic configuration near the vacancy, the precise position of the vacancy-related quasibound state levels may depend on various factors such as tube size, presence of the multiwalls, and preparation conditions.

In the case of the double vacancy produced by removing two neighboring atoms, the conductance shows four dips as shown in Fig. 4(b). Because the double vacancy considered here preserves the mirror plane containing the tube axis as in the case of the Stone-Wales defect, the π

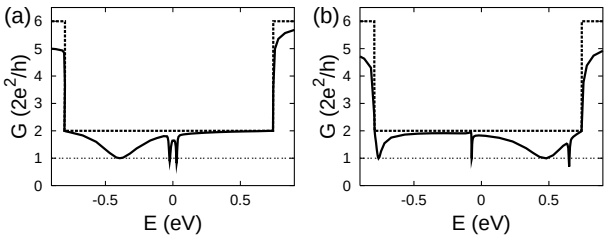

FIG. 4. Conductance of the $(10, 10)$ carbon nanotube with (a) a point vacancy or (b) a double vacancy.

and π^* bands are not mixed. All four dips correspond to almost complete reflection of either one of the π or π^* bands. The two very narrow dips, which are not found in the one π-orbital tight-binding model, are related to the dangling σ-bond states around the vacancy as in the case of the point vacancy.

In conclusion, we have performed first-principles calculations of conductance for metallic carbon nanotubes with substitutional impurities or structural defects, and arrived at a detailed understanding of the conducting behavior with these local defects. A substitutional boron or nitrogen impurity produces quasibound states of definite parity made of p orbitals perpendicular to the tube surface below or above E_F in close analogy to the acceptor or donor levels in semiconductors and the conductance is reduced at the corresponding quasibound state energies. A pentagon-heptagon-pair defect also produces two quasibound states and reduces the conductance by one quantum unit at the corresponding energies. In the case of a vacancy, valence electrons suffer resonant backscattering by quasibound states derived from the broken σ-bond states as well as the perturbed π states.

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